STUDIES OF THE CHEMISTRY OF ORGANIC BORON COMPOUNDS

BY

STANLEY MARSHALL PARMERTER

B. S., Greenville College, 1941

M. S., University of Illinois, 1942

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY IN THE GRADUATE SCHOOL OF THE UNIVERSITY OF ILLINOIS, 1944

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INTRODUCTION

The discovery that boron efficiently captures slow neutrons to become radioactive has stimulated a new interest in the synthesis of boronic acids. If a compound containing the boronic acid group could be caused to localize in tumor tissue, irridation of the area with slow neutrons would presumably destroy the tumor.

Boronic acids, as well as borinic acids and borines, generally are prepared by the reaction of alkyl borates with Grignard reagents. This is almost the only use of esters of boric acid in synthetic organic chemistry. The methyl ester, which is often superior in reactions of this type, has been much more difficult to obtain in the pure state than have its homologs.

One object of the present work was the synthesis of benzidines, containing one or more boronic acid groups, which could be used as intermediates in the preparation of boron-containing dyes similar in structure to dyes which are known to be preferentially absorbed by tumor tissue. It also seemed desirable to investigate new methods for the preparation of pure methyl borate and to explore other possible uses for alkyl borates in synthetic work.

DISCUSSION

The reported synthesis of *m*-nitrobenzeneboronic acid[1] was adapted to preparative work. This involved the treatment of phenylmagnesium bromide with butyl borate to give the dibutyl ester of benzeneboronic acid. The ester was hydrolyzed to benzeneboronic acid, which was nitrated with fuming nitric acid to give *m*-nitrobenzeneboronic acid. A zinc and alkali reduction of *m*-nitrobenzeneboronic acid has been used to prepare *m*-hydrazobenzeneboronic acid. However, all previous attempts to rearrange this compound to a benzidine had failed.[2] It has been possible to effect this rearrangement in small yields with either hydrochloric or sulfuric acid in aqueous or alcoholic solutions. Best yields were obtained when the reaction mixtures were heated at 50° for three hours.

By this method, a benzidine containing two boronic acid groups has been prepared. The synthesis may be outlined by the following reactions: phenylmagnesium bromide→dibutylbenzeneboronate→benzeneboronic acid → m-nitrobenzeneboronic acid → *m*-hydrazobenzeneboronic acid → 4,4′-diaminobiphenyl-2,2′-diboronic acid.

Analytical data indicate that the product has the composition of the desired benzidine. A proof of the structure was furnished by acetylation and subsequent removal of the boronic acid groups to give N,N′-diacetyl benzidine.

The tetrazonium salt of 4,4′-diaminobiphenyl-2,2′-diboronic acid was coupled with salicylic acid to give a dye containing the theoretical amount of boron. When the tetrazonium salt was coupled with phenol and β-naphthol, dyes were obtained which contained about half of the theoretical amount of boron. Great difficulty was experienced in the microanalysis of these compounds. A dye formed by coupling the tetrazonium salt of the benzidine with naphthionic acid had a neutral equivalent which indicated that all of the boron had been retained during the coupling reaction.

The known methods of synthesis of alkyl borates, when applied to the preparation of methyl borate, give an azeotropic mixture of the ester and methyl alcohol.[3] Since it is very difficult to separate the components of this mixture, a method was developed which did not employ methyl alcohol as a starting material. Alcohol-free methyl borate was obtained by an ester interchange between butyl borate and the methyl ester of a carboxylic acid. The reaction proceeded only in the presence of sodium methoxide; acids did not catalyze the interchange. Methyl benzoate, dimethyl phthalate and dimethyl oxalate were all satisfactory for use in this reaction, but methyl esters of acids containing α-hydrogen atoms gave poor yields of pure methyl borate.

When *n*-butyl borate was used to alkylate benzene in the Friedel-Crafts reaction, a mixture of isomers was obtained. The origin of these isomers was indicated by a study of the reaction of *n*-butyl borate with aluminum chloride. When the alkyl borate was heated with aluminum chloride, a mixture of

2-butene, *n*-butyl chloride and *s*-butyl chloride was obtained.

The observation that esters of boric acid undergo rapid hydrolysis suggested a study of their use as dehydrating agents. However, it was found that transesterification was the principal reaction when alkyl borates were heated with hydroxy compounds.

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[2] Weaver and Snyder, private communication.
[3] Etridge and Sugden, J. Chem. Soc., 989 (1928).

VITA

The author was born in Rochester, New York, on October 24, 1920. He graduated from the high school department of the A. M. Chesborough Seminary in June, 1937. In September, 1937, he matriculated in the collegiate department of the same institution. In September, 1939, he transferred to Greenville College, where he was granted the B.S. degree in June, 1941.

He was enrolled in the Graduate School of the University of Illinois from the fall of 1941 to the fall of 1944. In June, 1942, the degree of Master of Science was conferred on him. At the University of Illinois he was a University scholar from 1941 to 1942 and a teaching assistant from 1942 to 1944.

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